Water Assisted Growth of Two-Dimensional MoS$_2$/MoSe$_2$ Vertical Heterostructures on Molten Glass

Qian Cai$^{a,b}$, Qiankun Ju$^{a,b,c}$, Wenting Hong$^{a,b}$, Chuanyong Jian$^{a,b,c}$, Taikun Wang$^{a,b}$, Wei Liu$^{a,b}$

$^a$CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, PR China

$^b$Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, P. R. China

$^c$University of Chinese Academy of Sciences, Beijing, 100049, PR China.

E-mail: liuw@fjirsm.ac.cn

Experimental Section

1. CVD Synthesis of MoS$_2$ Monolayers

A two-zone CVD horizontal quartz tube furnace was employed to grow MoS$_2$ monolayers. Sulfur powder (320 mg) was placed in upstream zone 1. The Mo foil was ultrasonically cleaned in acetone, ethanol, and water for 15 min, respectively. The pretreated Mo foil was placed above the soda-lime glass substrate in a parallel geometry with a gap of 6 mm in the downstream zone 2. Before heating, 400 sccm Ar was flowed into the tube for 15 min to ensure a stable chemical reaction environment. Then the flow rate of Ar was controlled at 30 sccm for the following process. The temperature of zone 1 and zone 2 were heated to 200 °C and 720 °C in 35 min, respectively, and kept at that temperature for 4 min under an argon atmosphere. Herein, water vapor was introduced into the furnace by Ar carrier gas to synthesize large scale uniform MoS$_2$ Monolayers.

2. CVD Synthesis of vertical MoS$_2$/MoSe$_2$ heterostructure

The MoS$_2$/MoSe$_2$ vdW heterostructures were fabricated using a sequential CVD method similar to the growth of MoS$_2$ Monolayers. The proper ratio of S (320 mg) and Se (90 mg) mixture powder are put in the upstream zone 1. The pretreated Mo foil was placed faced down on the soda-lime glass substrate in a parallel geometry with a gap of 6 mm in the downstream zone 2. Before heating, 400 sccm Ar was flowed into the tube for 15 min to ensure a stable chemical reaction environment. Then the flow rate of
Ar was controlled at 30 sccm for the following process. The temperature of the zone 1 was heated to 200 °C in 35 min and kept at this temperature for 4 minutes for the growth of MoS$_2$ monolayers. Then the temperature quickly heated to 250°C in 4 min and keep for 4min for Se evaporation. The temperature of zone 2 was heated to 750 °C in 35 min and kept at this temperature for 12 minutes. After growth, the furnace was rapidly cooled to 400 °C to prevent additional reactions and then cooled down to room temperature. Eventually, epitaxially grown vertical MoS$_2$/MoSe$_2$ vdW heterostructures were obtained on the glass substrate.


The synthesized MoSe$_2$/MoS$_2$ heterostructures can be transferred onto any substrates (SiO$_2$/Si or soft substrate) using a modified poly(methyl methacrylate) (PMMA)-based wet transfer method. The MoS$_2$/MoSe$_2$ heterostructures substrate was spin-coated with PMMA and was baked at 120 °C for 3 min. Then makes cracks along the edge of PMMA/MoSe$_2$/MoS$_2$ with a knife. Subsequently, the PMMA/MoSe$_2$/MoS$_2$ film will delaminate from the glass substrate after injecting water due to their different surface energies. Floating PMMA/sample films in water were scooped with the target substrates. We then immersed the substrates in acetone to remove PMMA films.

4. Structure and Composition Characterization

Optical images of the MoSe$_2$/MoS$_2$ heterostructures were taken on an optical microscopy (Nikon, LV150N). Atomic force microscopy (AFM) images were acquired with a Bruker Dimension Icon operating in ScanAsyst mode using Bruker ScanAsyst-Air probes (silicon tip; silicon nitride cantilever, spring constant: 0.4 N·m$^{-1}$, frequency: 70 KHz). The images were analyzed using NanoScope Analyst software (version 1.40). Raman and PL measurements were performed on Invia Reflex micro-Raman spectroscope with 532 nm laser at room temperature. Raman spectra were calibrated by the Raman shift of single-crystal silicon at 520.4 cm$^{-1}$. Raman measurements were conducted using an 1800 g/mm grating to disperse the signal and generate a spectral resolution of less than 1 cm$^{-1}$ (a 600 g/mm grating was used for PL measurements).

5. Methods for TEM Characterizations

For the TEM specimen preparations, we transferred the synthesized MoSe$_2$/MoS$_2$ heterostructures onto Cu grids using a modified poly(methyl methacrylate) (PMMA)-based wet transfer method. The MoSe$_2$/MoS$_2$ heterostructures substrate was spin-coated with PMMA and was baked at 120 °C for 3 min. Then makes cracks along the edge of PMMA/ MoSe$_2$/MoS$_2$ with a knife. Subsequently, the
PMMA/MoSe$_2$/MoS$_2$ film will delaminate from the glass substrate after injecting water due to their different surface energies. Floating PMMA/sample films in water were scooped with a TEM grid (Holey carbon coated with 400-meshed Cu). We then immersed the grids in acetone to remove PMMA films. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and scanning-TEM (STEM) imaging were performed with FEI Tecnai F20 microscope with an accelerating voltage of 200 kV. For the SHG measurements, a mode-locked Ti:sapphire laser (Tsunami HP) centered at 800 nm (≈100 fs, 80 MHz) was amplified by a regenerative amplifier system (Spitfire Ace-PA-100, 1 kHz). And the resulting signal was collected by the above Raman system with a 100× objective. For the polarization-dependent SHG measurements, the signal was recorded every 10° of rotation of the sample in all 360° angles.

6. Fabrications and Measurement of the MoS$_2$/MoSe$_2$ Devices

For the device fabrication, the MoSe$_2$/MoS$_2$ vdW heterostructures are first transferred to a SiO$_2$ (300 nm)/Si substrate. Then, a layer of MMA copolymer was spin-coated on the TMDs heterostructures, followed by a 1 min bake at 160 °C on the hot plate. After this, another layer of PMMA was spin-coated on the substrate followed by a 5 min bake at 160 °C. Electron beam lithography was employed to define the drain and source electrodes by an 80 seconds XeF$_2$ etching. After the conventional development process, Ti/Au metal layer (10 nm/100 nm) was deposited to form the source-drain electrodes by electron beam evaporation and finally followed by a lift-off process with acetone. All of the devices are annealed at 5×10$^{-6}$ mbar, 420 K for 2 hours to reduce contact resistance and remove absorbed moisture. The electrical and optoelectronic properties of the heterostructures were measured in a vacuum with the Lake Shore Probe Station and Keithley 4200 semiconductor analyzer at room temperature.

7. Calculation of carrier mobility

For the calculation of carrier mobility, the method used is to measure the leakage current in the linear region at low $V_{ds}$. Then according to the following formula,

$$\mu = \frac{g_m}{C_{ox} V_{ds}} \cdot \frac{L}{W}$$

where $g_m = \frac{\partial I_{ds}}{\partial V_{gs}}$, which is the slope of the linear region of the $I_{ds}$-$V_{gs}$ curve; $V_{ds}$ is the drain voltage;
\[
\frac{\varepsilon_0 \varepsilon_{r1}}{C_{ox}} = \frac{d_{ox}}{L}, \quad \text{where} \quad \varepsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}, \quad \varepsilon_{r1} = 3.9, \quad \text{and} \quad d_{ox} (SiO_2) = 90 \text{ nm}; \quad \text{and} \quad L \text{ and } W
\]
are the length and width of the channel, respectively.

8. DFT Calculation Details

DFT calculations have been carried out in AtomistixToolKit (ATK) 2019.0 with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation within the generalized gradient approximation (GGA). We employ a 5 \times 5 \times 1 Monkhorst-Pack k-point grid with the cutoff energy of 50 Hartree. A repeating sheet model consisting of a 4 \times 4 lateral periodicity of TMDs was used.

Supplementary Figures

![Figure S1](image.png)

**Figure S1.** (a) XRD patterns of Mo foils after CVD process with and without the assistance of H_2O.
Figure S2. OM images of the as-prepared MoS$_2$ crystals on glass substrate with different Ar/water vapor flow rate. (a) 10 sccm, (b) 30 sccm, (c) 50 sccm, (d) 70 sccm.

Different Ar/water vapor flow rate of, 30sccm, 50sccm, and 70sccm was injected into the furnace as shown in Figure S2. In a mild H$_2$O concentration (mild oxidization of the Mo foil), the size of MoS$_2$ increased as the increasing concentration of H$_2$O from 10 to 30 sccm, which is due to the gradually increased oxidization of the Mo foil and sufficient supply of the MoO$_x$ precursor. When excess H$_2$O is introduced into the furnace (flow rate >50 sccm), the etching effect will be occurred on MoS$_2$ (Figure S2c), eventually leading to the formation of cracked samples (Figure S2d).
**Figure S3.** OM images of the as-prepared MoS$_2$ crystals on glass substrate with different gap distance between the Mo foil and the glass substrate. (a) 10 mm, (b) 8 mm, (c) 6 mm, (d) 2 mm.

The large gap distance between the Mo foil and the glass substrate lead to high sulfur concentration over the gap region. It can be seen that plenty of triangular MoS$_2$ is formed on glass substrate with the gap of 10 mm (**Figure S3a**), the small size of products is due to the high sulfur concentration and high nucleation density. When the gap is decreased from 10 to 6 mm (**Figure S3a-c**), the gradual reduction in sulfur concentration over the gap region is happened, which suppressed the nucleation density and increases the size accordingly. However, when the gap is further reduced to 2 mm (**Figure S3d**), irregularly shaped crystals formed due to the insufficient feeding of the S precursor, similar to the published report (*Nat. commun.* 2018, 9, 979.).
Figure S4. (a) OM images of the as-prepared MoS$_2$/MoSe$_2$ heterostructures on glass substrate. (b) OM images of the as-prepared MoSe$_2$/MoS$_2$ heterostructures on SiO$_2$/Si substrate. (c) SEM image of the as-prepared MoSe$_2$/MoS$_2$ heterostructures on SiO$_2$/Si substrate.

Figure S5. OM images of six representative MoSe$_2$/MoS$_2$ heterostructures with different Se reaction time of (a) 0 min, (b) 3 min, (c) 4 min, (d) 5 min, (e) 6 min and (f) 7 min, respectively. Scale bar: 5μm.
Figure S6. (a) OM image of the prepared MoS$_2$/MoSe$_2$ heterostructure on glass substrate with excess Se precursor. (b) SEM image of the prepared MoS$_2$/MoSe$_2$ heterostructure on Si/SiO$_2$ substrate with excess Se precursor.

Figure S7. Energy Dispersion Spectroscopy (EDS) of heterostructure collected from the MoS$_2$ monolayer (a) and MoSe$_2$/MoS$_2$ bilayer (b), respectively. The EDX spectrum for MoS$_2$ monolayer (Figure S7a) revealed that only the existence of Mo and S elements with the Mo:S atomic ratio of 1:2, and there are no Se signal can be detected. Besides, the EDX spectrum collected from MoSe$_2$/MoS$_2$ bilayer (Figure S7b) presents the atomic ratio of Se:S is 1:1. The element analysis results further demonstrated that both the MoS$_2$ and MoSe$_2$ is pure phase without S or Se doped.
Figure S8. (a) The schematic of MoS$_2$/MoSe$_2$ field-effect transistor (FET), multi-electrode backgate field-effect transistors (FETs). (b) The optical image of a typical MoSe$_2$/MoS$_2$ FETs. Electrodes E1, E2, E5 and E6 were deposited on the top of the stack MoSe$_2$/MoS$_2$, while E3 and E4 on top of the monolayer MoS2. Hence, three kinds of device channels were formed, (1) Monolayer MoS$_2$ channel (electrodes E1 and E2), (2) bilayer MoSe$_2$/MoS$_2$ channel (electrodes E5 and E6) and (3) bilayer MoSe$_2$/MoS$_2$-monolayer MoS$_2$ channel (electrodes E3 and E4), respectively. (c) Transfer characteristics of back-gated bilayer MoSe$_2$/MoS$_2$ FET and bilayer MoSe$_2$/MoS$_2$-monolayer MoS$_2$ FET.